

Section 4

Data Collection, Analysis, and Interpretation

Section 4 presents an overview of the RI data collection efforts and the methods of data analysis. Sections 4.1 and 4.2 discuss the two phases of the data collection. The general procedures for data collection are outlined in Section 4.3. Section 4.4 summarizes how COPCs were determined. The analytical program is discussed in Section 4.5. Section 4.6 discusses the data quality assessment. Deviations from the Phase I and II sampling events and their impacts are presented in Section 4.7. Data set development and interpretation for the nature and extent investigation is presented in Section 4.8.

4.1 Phase I of the RI

4.1.1 Program Overview

Phase I of the RI was designed to determine the nature and extent of organic and inorganic contamination within the Calcasieu Estuary and to support risk characterization. This phase of investigation was conducted on an AOC-by-AOC basis and included:

- Historical data evaluation
- Sample location selection using EPA's fully-integrated environmental location decision support (FIELDS) software
- Sediment and surface water sampling
- Data analysis

4.1.1.1 Historical Data Evaluation

Numerous historical data exist from a variety of characterization programs conducted by state and local agencies, as well as private industry within the Calcasieu Estuary. Phase I was initiated with a detailed evaluation of the existing chemical data maintained by EPA and NOAA (Section 1.2). A decision was made by the stakeholders to use all of the post-1992 data. It was assumed that these data were collected and analyzed under more stringent collection and analytical testing protocols. Pre-1992 data, although maintained by EPA and NOAA, were not used in the RI planning because of unknown quality.

The data were used to determine the occurrence, concentration, and mean and mean variance of COPCs as well as the number of samples with previously detected analytes. Data were also used to ascertain the number of samples needed for a statistically valid sampling program based on confidence interval/relative error ranges of 70/30 percent and 80/20 percent, which equate to 0.7 and 0.8 statistical

power, respectively. Given a mean and a standard deviation, an iterative set of three equations, as described by Gilbert (1987), was used to calculate the number of samples required to achieve the pre-specified confidence and precision.

4.1.1.2 Sample Location Selection

The number of samples calculated using the above-referenced method was then input into FIELDS as criteria to identify sample locations. For logistical considerations, the four AOCs (i.e., Bayou d'Inde, Bayou Verdine, Upper Calcasieu, and Lower Calcasieu [Figure 2-2]) were subdivided into multiple reaches. These reaches were arbitrary subdivisions based on general physical characteristics (e.g., industrial area, associated marshes, incised channel, etc.). To locate sampling points, FIELDS subdivided each AOC into equal area grids based either on the number of available samples or on the maximum diameter of an area with unacceptable concentrations of contaminants (i.e., hot spots) that would be left uncharacterized by the sampling effort. Once subdivided into grids, FIELDS selected a sampling point in the center of each equi-area grid cell. Randomness was introduced through the selection of a random starting node within a grid cell. The same node was then applied to all grid cells (a systematic-stratified sampling approach). FIELDS established coordinates for each sampling location. Sampling locations for Phase I are shown in Figures 4-1 through 4-3 and are labeled based on the AOC and reach in which the sample was located.

4.1.1.3 Sediment and Surface Water Sampling

Phase I RI sampling was conducted from December 1999 through March 2000. Field samples consisted primarily of sediment samples. Surface water samples were collected (and co-located with sediment samples) at approximately 20 percent of the

| Phase I Surface Sediment Locations | Phase I Multi-Depth Sediment Locations |
|--|--|
| <ul style="list-style-type: none"> ■ 63 in Bayou Verdine ■ 235 in Bayou d'Inde ■ 137 in Lower Calcasieu ■ <u>100 in Upper Calcasieu</u> <p>535 Total Locations</p> | <ul style="list-style-type: none"> ■ 7 in Bayou Verdine ■ 3 in Bayou d'Inde ■ <u>6 in Upper Calcasieu</u> <p>16 Total Locations</p> |

sediment sample locations. Sediment samples for chemical and physical analyses were collected from the surface (0 to 10 cm) and subsurface at multiple-depth intervals (0 to 10, 10 to 20, and 20 to 30 cm). Multi-depth sediment sample locations were determined from historical data and SVOC data. Bayou Verdine was the exception where surface samples were collected from 0 to 15 cm, and multi-depth locations were collected at intervals of 0 to 15, 15 to 30, and 30 to 45 cm to coincide with a previous nature and extent investigation conducted by one of the private industries located along the bayou.

Surface water samples were collected from a mid-depth of the water column or from multiple depths (i.e., one-third/two-thirds depth of the water column). Multi-depth surface water samples were collected if stratification of the water column was evident at any location based upon field measurements (salinity, dissolved oxygen, and

conductivity). Analyses included both chemical and physical parameters. More detailed information can be found in the site-specific sampling and analysis plans (SAPs) for each AOC (CDM 1999a, 1999b, 1999c, and 1999d).

Phase I data reduction and analysis identified the need for a second phase of sampling to minimize data gaps existing in Phase I, including resampling areas of poor data quality and supporting the

ecological risk assessment.

4.1.2 Ecological Assessment Site Reconnaissance

An ecological assessment site reconnaissance was conducted April 2000 through May 2000 to:

- Determine ecological tissue sampling methods appropriate for the estuary conditions
- Evaluate the nature of biota, sediment, and surface water within an ecological reference site
- Locate a suitable reference site to compare background conditions with the Calcasieu Estuary
- Collect tissue, in both the Calcasieu Estuary and reference sites, to determine the presence or absence of specific species and better understand the various trophic level relationships

4.1.2.1 Calcasieu Estuary Sampling

Tissue sampling locations were determined in the field based upon locations where fish are typically caught or collected in the various AOCs. Multiple locations were sampled in three of the four AOCs to determine a spatial distribution of some species (Figure 4-4).

Phase I Ecological Recon Tissue (T) Samples Collected

- 17 in Bayou d'Inde
- 18 in Lower Calcasieu
- 14 in Upper Calcasieu

Sediment and surface water samples were collected at the same locations and were co-located with shellfish sample locations. Sediment was collected to a depth of 15 cm whereas surface water was collected at midway of the water column.

**Phase I Ecological Recon
Sediment (SE)/Surface Water (SW)
Samples Collected**

- 1 SE/SW in Bayou d'Inde
- 1 SE/SW in Lower Calcasieu
- 1 SE/SW in Upper Calcasieu

4.1.2.2 Reference Area Selection and Sampling

An objective of the ecological reconnaissance was to locate a suitable reference area for Phase II of the RI. Requirements for the reference area were:

- Similar habitat, substrate, and water quality conditions to the Calcasieu Estuary
- No known industrial point sources of contaminants in the area

Data collected from a suitable reference area would allow comparisons to be made between the Calcasieu Estuary and an area unaffected by industrial development. This provided another screening level in addition to screening levels used in the HHRA and the BERA. The reference areas are further discussed in Section 6 where data are presented that describe the physical and chemical characteristics and discuss the suitability of using these areas for comparisons.

**Phase I Ecological Recon
Reference Area Samples Collected**

- 3 SE / 1 SW in Reference Area
- 15 T in Reference Area

During the field investigation, Johnsons Bayou (Figures 2-1 and 4-5) exhibited conditions similar to Calcasieu Estuary and was chosen as the location to collect tissue, sediment, and surface water.

4.2 Phase II of the RI

4.2.1 Program Overview

Phase II of the RI was a more focused characterization of contaminant levels in sediment, porewater, and biota tissue (i.e., fish and invertebrates), as well as evaluation of sediment toxicity, porewater toxicity, and benthic invertebrate community structure. The objectives of the Phase II RI were to:

- Minimize data gaps identified in the Phase I nature and extent data collection
- Collect additional information from designated reference areas
- Support the BERA and HHRA
- Conduct a sediment quality triad (SQT) to determine the relationship between sediment chemistry and toxicity to support an evaluation of the ability of the

sediment quality guidelines (SQGs) to correctly classify sediments in the study area as toxic or not toxic

- Provide data necessary to evaluate the risks to sediment-dwelling organisms associated with exposure to contaminated sediments
- Provide data necessary to evaluate the risk to fish and wildlife resources that are associated with consumption of contaminated prey items

4.2.1.1 Minimize Data Gaps

Several data gaps were identified in the Phase I data. Elevated detection limits, confirming reported data in some areas, and refinement of vertical and horizontal extent of contamination in specific areas required the collection of additional samples. Phase II surface sediment samples were collected at pre-selected locations to refine the horizontal extent of contamination around specific sites in the estuary and verify reported detections and non-detections. Vertical profile samples (multi-depth) were

Phase II Data Gap Sample Locations

- 18 (14 multi-depth) from Bayou d'Inde
 - 6 (2 multi-depth) from Upper Calcasieu
 - 9 (1 multi-depth) from Lower Calcasieu
- 33 (17 multi-depth) Data Gap Locations

collected to determine vertical extent of contamination at intervals of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm. These determinations allow evaluation of the impact that remediation (e.g., excavation), dredging, or natural processes (e.g., storms)

may pose through re-suspension of COPCs. The multi-depth samples were collected at pre-selected Phase I locations where elevated COPCs were detected. Sample locations are shown in Figure 4-6.

Thirty-three locations were sampled for nature and extent delineation purposes during Phase II. Surface sediment samples were collected at the 10-cm interval. Multi-depth samples were collected at intervals of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm. Samples were collected during December 2000.

4.2.1.2 Sediment Quality Triad

The SQT integrates information on sediment toxicity, chemistry, and benthic community structure in an integrated weight-of-evidence approach (Ingersoll et al. 1997). The SQT was designed to provide the information that is required to evaluate the risks to sediment-dwelling organisms that are associated with exposure to contaminated sediments. This is accomplished from the evaluation of whole-sediment and porewater toxicity effects on benthic invertebrate community status, both of which support direct evaluations of the effects of contaminated sediments on benthic organisms. In addition, the information generated will be used to evaluate if the SQGs developed for the Calcasieu Estuary correctly classify sediments in the study area as toxic or not toxic. Importantly, the data collected will provide the information to develop site-specific linkages between sediment chemistry and biological effects.

The field effort involved the collection of samples from 100 SQT locations. Sediment chemistry and benthic community structure were determined at all 100 locations, whereas only 50 locations had matching porewater chemistry.

The locations of the sampling stations were determined using a quasi-stratified random sampling design. The study area and candidate reference areas were divided into 51 reaches, which typically represented a recognizable topographic feature, such as a lake, a waterway, or a portion of a waterway in which conditions were expected to be relatively consistent. In the lakes, deeper waters (> 1 m) were excluded from consideration to facilitate co-location of the sediment sampling stations with the fish sampling stations. Subsequently, roughly 100 samples were distributed among the various reaches in a manner that provided broad geographic coverage of the study and reference areas.

In total, 31 areas within the estuary (Figure 4-7 through 4-11) and reference areas were sampled (Figures 4-12 through 4-13). The 31 areas and their corresponding sample locations (including reference areas) were designed by considering the distribution of sediment samples with various chemical characteristics (i.e., using data from the Phase I sampling program, historical data, and evaluating the sediment chemistry

Phase II SQT Sample Locations

- 31 from Bayou d'Inde
 - 10 from Bayou Verdine
 - 15 from Lower Calcasieu
 - 29 from Upper Calcasieu
 - 15 from Reference Areas
- 100 SQT Locations

data using mean effects range-medium [ERM] quotients). As such, the sediment samples were collected to have a broad range of chemical characteristics. This broad distribution of sediment chemistry will support logistic regression modeling of the matching sediment chemistry and sediment toxicity data, thereby

facilitating comparison to the models that have been established for other areas in North America (Field et al. 1996; MacDonald et al. 2000a,b). For a more detailed explanation of the sampling design and strategy, see the *Phase II Sampling and Analysis Plan*, (CDM 2000a).

4.2.1.3 Tissue Collection

The objectives for collecting tissue during the Phase II sampling included (1) evaluating the risks to human health by quantitatively measuring contaminant concentrations in fish and invertebrates likely to be consumed and (2) evaluating the risk to ecological receptors by quantitatively measuring the contaminant concentrations.

The Phase II sampling design evaluated the BERA and HHRA data needs to determine the type of species and the quantity to be collected. The types and quantity of species to be collected were based upon evaluating the feeding ecology of the fish and wildlife focal species and their likely foraging areas.

Phase II Tissue Samples

- 251 from Bayou d'Inde
- 133 from Lower Calcasieu
- 202 from Upper Calcasieu
- 138 from Reference Areas
724 Tissue Samples

The prey groups were selected based on assessment endpoints developed from the ecological assessment data quality objective (DQO) workshop (MacDonald et al 2000a), the *Problem Formulation Technical Memorandum, Baseline Ecological Risk Assessment - Calcasieu Estuary* (CDM 2001), input from the human health risk assessors, and USFWS.

The estuary supports a large variety of fish and invertebrate species that are prey for the wildlife focal species. The area where these species feed and live varies (e.g., sheltered bayous versus open water). Likewise, the degree to which they travel the estuary to breed also varies. To ensure these variables were represented, the prey groups were separated into groups as shown in Table 4-1. The species in each of the identified prey groups were interchangeable as the focal species predators since they will be unlikely to have distinct preferences for one species over another.

Sampling of prey that may move from one area of the estuary to another (i.e., groups 2 through 5) was needed to estimate exposure estimates for other wildlife focal species (e.g., osprey, dolphin). As the prey from these groups feed from larger areas across the estuary and their tissue concentration is less variable, a less detailed (estuary-wide collection versus area specific) sampling was needed for both the BERA and HHRA.

All tissue sample locations, with the exception of blue crab locations, were paired as closely as possible to SQT locations. At each of the stations (Figure 4-10, 4-11, and 4-13), multiple samples of group 1 fish and invertebrates (i.e., 3 to 5 samples of each sub-group) were collected within a 100-m radius of the SQT coordinates. The area sampled for groups 2, 3, 4, and 5 was expanded to 500 m. Several SQT sample locations did not provide adequate fish populations; so pre-selected alternate locations in that area were used.

Whole body samples from each prey group were used for the BERA, whereas a subset of group 4B fish was filleted for the HHRA.

Tissue collection occurred between October 2000 and December 2000. All sampling was conducted in accordance with the *Phase II SAP for RI/FS of Calcasieu Estuary Cooperative Site* (CDM 2000b).

4.3 Data Collection Methods

Collection methods used in Phases I and II of the RI varied by the analyses required (chemical and/or bioassays), types of media, and depth of sediment to be collected. All sample locations (with the exception of the ecological assessment reconnaissance) were determined prior to field mobilization using FIELD5. Universal transverse mercator (UTM) coordinates for each sample location were uploaded from FIELD5 to

a differential global positioning system (GPS) receiver that allowed navigation to each sample station. Actual UTM coordinates were established while sampling at each sample location with a positional accuracy of the GPS unit of less than 1 m.

General sampling procedures included the following steps for sediment, surface water, and tissue:

- All field monitoring equipment was calibrated daily in accordance with manufacturers' instructions and CDM standard operating procedures (SOPs) (CDM 2000b). All calibration information was recorded either in the applicable logbook or on calibration sheets.
- Sampling locations had predetermined coordinates that were navigated to using a differential GPS unit. Daily sampling efforts generally progressed from downstream to upstream locations to avoid cross contamination of the water samples. In isolated cases, this was not possible, but care was taken to limit the potential for cross contamination.
- Low-draft boats were stabilized by deploying a metal rod (spud) into the sediment on opposite corners of the boat if sediment and surface water samples were to be collected. Sampling was conducted away from where spuds may have disturbed sediment. If the locations were inaccessible from the boat due to low water, samplers would walk to the location. Boat stabilization was not needed for tissue sampling.
- The surface water column thickness was measured from a downstream location on the boat.

The samples were then collected as described in Sections 4.3.1 through Section 4.3.5.

4.3.1 Sediments

All sampling was conducted in accordance with the procedures specified in the *Phase I Sampling and Analysis Plans for Bayou Verdine* (CDM 1999a), *Bayou d'Inde* (CDM 1999b), *Lower Calcasieu* (CDM 1999c) and *Upper Calcasieu* (CDM 1999d), and *Phase II Sampling and Analysis Plan* (CDM 2000b) unless otherwise noted in Section 4.7 Deviations from Sampling and Analysis Plans.

Sediment sampling followed these general steps:

- Sediment sampling equipment was set up as described in CDM SOP 1-1 Section 5.4 (CDM 2000b). The top of sediment and sample interval to be collected was initially marked on the push rod so that the deployment depth could be defined.
- Sediment was collected at predetermined depths in accordance with CDM SOP 1-1 Section 5.4 (CDM 2000b). If the sample was for whole chemistry only, the sample was placed in a stainless steel bowl prior to sub-sampling.

- If VOC analysis was required, an aliquot of the sample was immediately placed in appropriate containers. Otherwise, the samples for whole chemistry (only) were homogenized using stainless steel mixers and bowls prior to placement in appropriate containers.
- An aliquot was also set aside for physical testing. All sediment samples were screened for VOCs using a photoionization detector (PID).
- If the sample was for the SQT, each replicate was sub-sampled for benthic community surveys prior to placement in acid washed, high-density polyethylene (HDPE) containers. SQT samples were sealed in containers and transported to the field office for homogenization and sub-sampling into containers for whole sediment chemistry and toxicity testing.
- Once sub-sampled, all sample containers were placed in ice chests or the sample refrigerator and cooled to 4°C plus or minus 2°C.
- Sediment lithology was logged in accordance with CDM SOP 3-5 (CDM 2000b). Physical parameters were logged on field sheets and/or the logbooks.
- Sediment sampling equipment, upon completion of a station, was rinsed in the surface water at the sampling location. Once rinsed, equipment was decontaminated on the boat in accordance with CDM SOP 4-5 (CDM 2000b) and wrapped in foil. All decontamination and rinse waters were retained for disposal at a Lake Charles POTW.
- Shallow sediment samples were collected using a 15-cm or 23-cm Eckman Dredge grab sampler from the upper 10 cm of the sediment surface. The 15-cm sampler was used to collect sediment for sediment chemistry only, whereas the 23-cm sampler was used for the sediment chemistry, porewater chemistry, and toxicity testing.
- Penetration into the substrate was accomplished by pushing the Eckman to the desired depth, not to exceed 10 cm. On average, one to four grabs were required to obtain sufficient volume for the SQT.
- Sediment samples collected from the 0 to 30-cm depth were obtained with a decontaminated, stainless steel push tube sampler. Sample was extruded from the coring device and separated into multi-depths (0 to 10 cm, 10 to 20 cm, 20 to 30 cm). Multiple replicates were homogenized to collect adequate volume for analyses. Because of the small diameter of the coring device, on average, 4 to 10 grabs were required to obtain sufficient volume.

4.3.2 Surface Water

Both shallow and deep surface water samples were collected from the Calcasieu Estuary based upon salinity concentration gradients. Surface water samples were

collected midway in the water column unless salinity stratification was measured (i.e., 0 to 0.5 ppt, 0.5 to 5 ppt, 5 to 18 ppt, 18 to 30 ppt, and > 30 ppt). If salinity stratification existed, a sample was collected from the middle of each zone. All surface water samples were co-located with surface sediment samples. Surface water samples were collected prior to sediment sampling and followed these general procedures:

- A peristaltic pump with clean tubing was set up as described in CDM SOP 1-1 Section 5.3.2 (CDM 2000b). The length of the tubing from the pump was either equal to the depth of water column, if more than one salinity zone existed, or to the mid depth of the water column if unstratified. Tubing was marked for depth control.
- Salinity was measured prior to sampling to determine if a salinity gradient existed.
- Other conventional parameters (e.g., TSS, dissolved oxygen [DO], ORP, etc.) were measured at the location where the sample was collected. In some instances, multiple measurements were recorded if determining a salinity gradient.
- The pump was allowed to purge for at least 2 minutes prior to collecting a sample for physical testing beginning with the shallow surface water sample. Samples were collected at an approximate pumping rate of 1 liter/minute (L/min).
- Samples were collected at the determined depths in accordance with Sections 5.2 and 5.3 of CDM SOP 1-1 (CDM 2000b). All appropriate sample jars were filled directly from tubing except for dissolved metals. The sample for dissolved metals was collected last after placing a 0.45- μm filter in line with the tubing.
- Surface water samples were recorded in accordance with SOP 3-5 (CDM 2000b) and placed in a cooler with ice at 4°C plus or minus 2°C. Physical parameters were logged on field sheets and/or the applicable logbook.
- Sampling equipment was decontaminated on the boat in accordance with SOP 4-5 (CDM 2000b). All decontamination and rinse water were retained for disposal at a POTW.

All sampling was conducted in accordance with the procedures specified in the *Phase I Sampling and Analysis Plan for Bayou Verdine* (CDM 1999a), *Bayou d'Inde* (CDM 1999b), *Lower Calcasieu* (CDM 1999c), *Upper Calcasieu* (CDM 1999d), and *Phase II SAP* (CDM 2000b) unless noted in Section 4.7 Deviations from Sampling and Analysis Plans.

4.3.3 Porewater

Porewater is the interstitial water present in the sediment. Porewater samples were collected at 50 locations as part of the SQT in Phase II. Sediment aliquots for

porewater collection followed the general procedures for sediment collection as described in Section 4.3.1.

Following collection, sediment for porewater analysis was placed into six 3.8-liter plastic containers and was sent to the laboratory to be extracted. Porewater was extruded by mechanical squeezing at the laboratory until the desired volume was collected. Samples were recorded in accordance with SOP 3-5 (CDM 2000b) and placed in a cooler with ice at 4°C plus or minus 2°C.

4.3.4 Benthic Community Survey

Benthic community survey samples were collected by using a sub-core from a 23-cm Eckman Dredge grab sampler used for the collection of SQT sediment samples. The cores were 6.72 cm diameter, covering an area of 35.4 cm². Five replicates were collected per SQT sample location, or one core was taken from each Eckman grab sample. Each replicate was then placed in a polyethylene container and transported to the field laboratory where samples were cleaned using a 0.5-millimeter (mm) sieve that prevented any loss of macrofauna. The remaining sample was then containerized and fixed with 5 percent buffered formalin solution, labeled, properly stored, and shipped to the laboratory. Once received in the laboratory, macrofauna were extracted and removed by hand sorting. The retained organisms were identified to the lowest possible taxa (generally species) and counted. Biomass was measured by combining the organisms into the following higher taxonomic groups: Crustacea, Mollusca, Polychaeta, Nemertinea, Ophiuroidea, and others, which includes all other rare taxa. Samples were placed on a tared aluminum pan, dried at 55°C for 24 hours, and weighed to the nearest 0.01 milligram (mg). No chemical analysis was performed on collected biomass. All quality assurance and quality control (QA/QC) procedures followed EPA's Environmental Monitoring and Assessment Program (EMAP) protocol (CDM 2000b).

4.3.5 Fish and Invertebrate Collection

Fish and invertebrate collection required the use of many different techniques and flexibility to collect the quantity of tissue required for the RI. The sampling methods included minnow traps, dip nets, mini-trawls, small oyster dredges, small-mesh seines, small trap nets, gill nets, and angling.

Samples to be used for the HHRA and BERA were conducted simultaneously. Fish samples needed for the HHRA were filleted, whereas samples needed for BERA were whole body. All samples were frozen and stored until the collection was completed to assess the need to collect additional samples to meet DQOs or to ensure that enough mass was collected for analysis.

Fish collected for the HHRA were also evaluated by the USFWS using the Biomonitoring of Environmental Status and Trends (BEST) program methods. These evaluations were done to support the USFWS natural resource damage assessment program. BEST methods identify contaminant effects on aquatic species. This

assessment program uses various methods (see Section 4.5.7 for further detail) to evaluate environmental stress on aquatic species.

4.4 Determination of Contaminants of Potential Concern

COPCs are determined in the RI as those chemicals that exist at concentrations or impart unacceptable risk to human health or the environment. COPCs for sediment, surface water, and tissue were initially identified by using historical data to evaluate human health risks associated with the release of hazardous chemicals into the Calcasieu Estuary (CDM 1999). This process involved the following steps using historical data:

- A statistical summary of the data for each medium was compiled, including range of detected concentrations, range of detection limits, and detection frequency of all chemicals analyzed.
- The maximum detected concentration was used as the screening concentration. If the constituent was not detected in any samples, the maximum reported detection limit was used as the screening concentration.
- Screening concentrations were compared to toxicity screening values to determine exceedences. Surface water toxicity screening values were selected from the lesser of the National Recommended Water Quality Criteria (Human Health Consumption of Organism Only) and Louisiana Ambient Water Quality Criteria. Tissue toxicity screening values were selected from EPA Region III risk-based concentrations for fish tissue. Sediment was not compared to a toxicity screening value. (Regional background values and applicable or relevant and appropriate requirements [ARARs] were not available at the time.)
- Chemicals with screening concentrations greater than the toxicity screening value were retained as COPCs.
- Contaminants detected at concentrations less than toxicity screening values, or with detection limits less than toxicity screening values, were eliminated as COPCs.
- Contaminants that did not have toxicity screening values were retained as COPCs for further evaluation unless these contaminants were not detected in any samples.

Upon conclusion of Phase I, the retained COPCs were re-evaluated using the recent data collected during the RI. Phase I chemicals were re-evaluated during a BERA workshop (MacDonald et al. 2000) by comparing measured concentrations to ecological water and sediment quality benchmarks to determine which COPCs and areas of potential concern would be investigated during Phase II. It was determined during the workshop that:

- For water-borne constituents, the contaminants that occurred in water samples at concentrations (i.e., total concentrations in unfiltered water samples) in excess of the final chronic value were considered ecological COPCs.
- Contaminants that occurred in whole sediments at concentrations in excess of ERM_s or probable effect levels (PEL_s) (MacDonald et al. 1996; Canadian Council of Ministers of the Environment 1999) were considered ecological COPCs.

In addition, initial preliminary remediation goals (PRGs) for protection of human health were developed based on data collected in Phase I and identified by the Calcasieu Estuary Team (CDM 2000b). PRGs were estimated by re-arranging the hazard or risk equation to solve for concentration. An acceptable hazard quotient was set to one, and the acceptable risk level was set to 10⁻⁵. The constituents identified in the BERA workshop and PRG developments were considered COPCs for Phase II.

Upon completion of Phase II, retained COPCs in sediment for human health risk were further refined in the draft HHRA (CDM 2002b). The COPC selection for the HHRA was accomplished using the following steps:

- For surface sediment (0 to 10 cm), all detected chemicals were carried forward to the evaluation.
- Chemicals that were detected very infrequently (i.e., in less than 5 percent of the samples) were not selected as COPCs.
- Chemicals that are essential nutrients (i.e., calcium, magnesium, potassium, sodium) were not selected as COPCs.
- Chemicals that were detected in greater than 5 percent of the samples and are not essential nutrients were screened against toxicity-based screening levels to identify the COPCs.
- Chemicals were considered COPCs if the maximum detected concentration exceeded the screening level or if there was no toxicity-based screening level available for comparison.

Table 4-2 lists the presently known COPCs for the Calcasieu Estuary based upon ecological and human health risks. Section 13 (BERA) and Section 14 (HHRA) provide detail into the development of contaminants that pose a risk to the ecology or human health.

4.5 Analytical Program

A variety of parameters were measured to evaluate the Calcasieu Estuary as well as determine the nature and extent of contaminants in sediment, surface water, and tissue. Table 4-3 lists the media and analytical protocol (i.e., analytes and methods). Table 4-4 lists sample volume/containers and the required preservation methods.

Phase I analytical methods were selected in accordance with the investigation's DQOs involving EPA's Contract Laboratory Program (CLP). Phase II analytical methods were determined by the DQOs. Physical and chemical analyses were performed using validated and standard methods in the environmental laboratory industry. A detailed description of the analytical protocols is presented in the following subsections.

4.5.1 Conventionals

Most media were analyzed for conventional and physical parameters in the laboratory and by field instruments. The physical analysis of sediments included examination of several parameters that included grain size, cation exchange capacity (CEC), and TOC. In addition, various field parameters were measured that included monitoring for VOCs by PID, ORP, soil stiffness, and color.

The physical parameters measured for surface water included pH, temperature, conductivity, salinity, DO, turbidity, ORP, total dissolved solids (TDS), and specific gravity. All of these parameters were quantified using a multi-function Horiba water quality meter.

Other conventional parameters for surface water that were analyzed include alkalinity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), hardness, TOC, TDS, TPH, bromide, chloride, fluoride, ortho-phosphate, sulfate, total Kjeldhal nitrogen (TKN), ammonia, and nitrate/nitrite.

Porewater was analyzed for dissolved organic carbon (DOC), ammonia, and hydrogen sulfide.

All tissue samples were analyzed for the percentage of lipids in the sample.

4.5.2 Inorganics

Inorganics were measured in sediment, surface water, porewater, and tissue for the RI. Various methods (Table 4-3) were used to quantify inorganics found in the estuary. The following inorganic analyses were performed for the RI:

- In Phase I, sediments were analyzed for Target Analyte List (TAL) metals and cyanide.
- In Phase II, sediments were analyzed for total recoverable metals (nickel [Ni], copper [Cu], zinc [Zn], silver [Ag], cadmium [Cd], and lead [Pb]).
- In Phase II, a limited number of predetermined sediment sampling locations were analyzed for toxicity characteristic leaching procedure (TCLP) metals and total recoverable metals.
- Acid volatile sulfide and simultaneously extracted metals (AVS/SEM) analysis was performed in Phase II at all sediment locations.

- Surface water samples were analyzed for total and dissolved TAL metals and cyanide by CLP. In addition, total and dissolved arsenic (As), Cu, Pb, and mercury (Hg) were analyzed using SW-846 7000-series analytical procedures (Table 4-3) (CDM 2000b).
- In Phase II, porewater samples were analyzed for total recoverable and dissolved metals.
- Tissue was analyzed for TAL metals and total Hg.

4.5.3 Organics

Various organics were measured in sediment, surface water, porewater, and tissue for the RI (Table 4-3). The following organic analyses were performed:

- Sediments were analyzed for VOCs, SVOCs, herbicides, pesticides, PCBs, PCB congeners (20 percent of Phase II sediment samples), TPHs, dioxins/furans (20 percent of sediment samples), methyl-mercury (Me-Hg), and TCLP SVOCs at predetermined locations.
- Surface water samples were analyzed for VOCs, SVOCs, herbicides, pesticides, and PCBs in Phase I.
- Porewater samples were analyzed for SVOCs, pesticides, and PCBs in Phase II.
- Tissue samples were analyzed for SVOCs, pesticides, and PCBs. Selected tissue samples were also analyzed for PCB congeners and dioxin/furans.

Required sample volume and container types are presented in Table 4-4. Due to the low sample volume in Phase I, some samples had elevated detection limits, which rendered data unusable. Analytical procedures were modified for Phase II such that a 50-gram (g) sample was used versus a 35-g sample (Phase I) for SVOCs for sediments (Method 8270) to meet the required detection limits.

4.5.4 Toxicity and Bioaccumulation Tests

Sediment toxicity tests were conducted for sediment collected at the 100 SQT locations. These tests were used to measure 10- and 28-day survival and growth endpoints with the amphipod *Hyaella azteca* and acute 10-day tests with the amphipod *Ampelisca abditi*, to measure survival. Sediment bioaccumulation tests were conducted with the polychaete *Nereis virens* to determine the bioavailability of sediment-associated contaminants.

The 10-day whole sediment tests were conducted following the procedures outlined in EPA's *Methods for Assessing the Toxicity of Sediment-Associated Contaminants with Estuarine and Marine Amphipods* (EPA/600/R-025; EPA 1994a). The 28-day bioaccumulation tests were conducted in accordance with the EPA and the USACE

Standard Testing Manual entitled: *Evaluation of Dredged Material for Proposed Ocean Disposal - Testing Manual* (EPA/503/8-91/001, February [EPA 1991]).

Microtox® was also applied to each SQT sediment sample to quantify potential effects on decomposers in sediments. This test determines the bioavailability of chemicals in sediments. The Microtox® solid-phase test exposes glowing luminescent bacteria (*Vibrio fischeri*) directly to sediment-bound chemical contaminants in an aqueous suspension of the test sample (Johnson and Long 1998). The endpoint measured in the solid-phase test with Microtox® is the EC50 (expressed as sediment wet weight/milliliter [mL]). An EC50 is the effective concentration value where an impact to 50 percent of the test population is observed.

A 28-day bioaccumulation test was conducted at 10 SQT locations (Figures 4-7 through 4-9) with the polychaete *Nereis virens*. The levels of metals, PAHs, PCBs, organochlorine pesticides, and other SVOCs were measured in the polychaete tissues at the conclusion of the test. Samples were sent to the laboratory where they were homogenized prior to analysis and were subjected to the same analyses as other tissue samples. The 28-day bioaccumulation test data will be used with the corresponding sediment chemistry data to estimate sediment-to-biota accumulation factors for the sediment areas.

Porewater toxicity tests conducted included sea urchin (*Arabcia punctulata*) fertilization and embryological development assays, macrophyte algal germination and growth (*Ulva spp.*) assays, and embryo-larval growth and survival assays with red drum (*Sciaenops ocellatus*). Methods for conducting porewater tests follow procedures described in Carr et al. (1996a,b; 1997) and Hooten and Carr (1998), and the American Society for Testing and Materials (ASTM 2000).

Results for the toxicity and bioaccumulation tests are summarized in Section 12 and presented in Section 13.

4.5.5 Benthic Community Survey

The benthic macroinvertebrate community survey was conducted across the entire estuary taken at the 100 SQT locations. The sample methods and analysis procedures were published in the *EPA-EMAP Protocol* (Paul et al. 1992).

An index of biotic integrity (IBI) was used to characterize benthic condition of the Calcasieu Estuary. This is a multi-metric index used widely by benthic ecologists to integrate numerous biotic responses, account for natural-habitat variations, and define reference conditions (Weisburg et al. 1997). Such indices have found wide acceptance among biologists and have been adopted for analyses of estuaries throughout the United States (Fore et al. 1996; Weisburg et al. 1997; van Dolah et al. 1999; Dauer et al. 2000; Llanso 2001; Alden et al. in press; Ranasinghe et al. in press).

Results for the benthic community structure are summarized in Section 11 and presented in Section 13.

4.5.6 Toxicity Identification Evaluation (TIE)

A parallel study was conducted by EPA under the Clean Water Act using TIE tests at SQT selected locations. The tests were limited to nine whole sediment locations across the estuary. Methods used are based upon the following EPA guidance: *Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I*, EPA/600/6-91/005 (EPA 1991b).

TIE evaluations typically consist of three phases: (1) characterize the physical/chemical properties of the toxicants; (2) identify the toxicants (typically non-polar organics, ethylene diamine triacetic acid (EDTA), chelatable metals, and ammonia); and (3) perform a final confirmation through a weight-of-evidence approach to effluent testing.

The whole sediment TIE methods performed on these samples consisted of three manipulations: (1) addition of a cation resin to remove metals, (2) addition of a powdered coconut charcoal to remove organics, and (3) exposure to the sea lettuce (*Ulva lactuca*) to remove ammonia. Results of the TIE are summarized in Section 11.

4.5.7 BEST Program

Fish selected for the HHRA, prior to fillet, were evaluated by the USFWS using the BEST program at the time of collection. BEST is a national program of the Biological Resources Division (BRD) of the USGS. BEST is specifically designed to focus on the response of biological resources to environmental contaminants. Under the BEST program, USFWS examined fish for deformities, skin lesions, or tumors on the surface and within the specimen in accordance with several USGS/BRD guidance documents (USGS/BRD 1999 and USGS/BRD 2000). Results of USFWS's evaluations were not available for inclusion in this RI.

4.6 Data Quality Assessment

The data used in this RI/FS and associated risk assessments were assessed through a data evaluation program that includes data validation and data evaluation in accordance with EPA's nationally recognized guidelines. Prior to use, this evaluation measure ensures quality of the data used is defined and that a known confidence in data usability is ensured. The data validation process addresses these needs.

This section provides a data quality review of the data collected for the RI report and addresses data usability. The study design, DQOs, and quality assurance project plan (QAPP) are outlined in the approved SAPs (CDM 1999a, 1999b, 1999c, 1999d, and 2000b).

4.6.1 Data Validation and Evaluation

Data validation was conducted to assess the quality of the laboratory data and to determine if it satisfies the project's DQOs. Data are compared to established criteria for categories such as data package and laboratory completeness and is completed after the laboratory has finished their review. During this process, individual sample

results are accepted, rejected, or qualified. Data that meet all the validation criteria are accepted as unqualified and can be used without discretion as needed. Data that are rejected (R) for not meeting one or more of the validation criteria cannot be used. Some data fall into the gray area between accepted and rejected. These data are qualified as estimated (J) to indicate that one or more of the validation criteria were not met (EPA 1994). Data validation may determine possible analytical error, but more importantly, it assesses data usability. Data are presented in sample delivery groups (SDGs) that typically includes:

- A narrative describing the samples analyzed, data and time of receipt, temperature and pH, and the presence of a chain-of-custody (COC) form
- A listing of procedures used in preparing the sample for analysis and the analysis methods
- Results of analyses
- Technical difficulties encountered that may affect the quality of the result
- Any instances where a sample may have been re-prepared or re-analyzed due to not meeting method or contract requirements
- Deviations from standard protocols
- An explanation of laboratory qualifiers used
- Signature of laboratory designee(s) for ensuring data quality and data package content

Data validation was performed in accordance with EPA's *Contract Laboratory Program National Functional Guidelines for Data Review* (both organic and inorganic) (EPA 1994a, b). Data collected for this RI were validated at different levels. Full data validation includes review of the raw data with error checks on laboratory performance, preparation of standards and samples, analyte identification, and re-quantification from raw data. Data evaluation (limited data validation) consisted of evaluating a set of quality control samples including laboratory control sample (LCS) analyses; matrix spike/matrix spike duplicate (MS/MSD) analyses; and method, field, and trip blanks. Data evaluation is an assessment of precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters. PARCC goals were established and defined for the project in the various SAPs. The following sections define and discuss these PARCC parameters, as well as sensitivity.

In Phase I, sample data from over 1,500 individual samples and 172 SDGs from six different CLP and subcontract analytical laboratories were received, reviewed, validated, and evaluated. One hundred percent validation and evaluation was performed on Phase I data. In Phase II, validation was reduced to SDGs if errors or problems were found during the data evaluation. This resulted in nearly 6,000

individual samples from Phase II being 100-percent evaluated. Seventeen percent of the 6,000 samples were validated. Table 4-5 and Table 4-6 summarize the data validation and evaluation of Phases I and II samples.

The data gathered from the RI investigation were determined usable through this data validation program and comply with EPA Region VI's *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual*, 1996. Full documentation of the validation process is located in CDM's Data Evaluation Summary Reports (CDM 2000a, CDM 2002a). Appendix B specifies the validation and evaluation criteria and percent recoveries for the Calcasieu Estuary RI.

4.6.1.1 Precision

The precision of a measurement is an expression of mutual agreement among individual measurements of the same property taken under prescribed similar conditions. Precision of the analysis is assessed by comparing original and duplicated sample results, where applicable. The relative percent difference (RPD) was calculated for each pair of applicable duplicate analyses using the following equation:

$$\text{Relative Percent Difference} = |S - D| / ((S+D) / 2) \times 100$$

Where:

S = First sample value (original value)
D = Second sample value (duplicate value)

Precision of reported results is a function of inherent field-related variability plus laboratory analytical variability, depending on the type of quality control (QC) sample. Data were evaluated for precision using the following types of samples (in order of priority): field duplicates, laboratory duplicates, LCS/laboratory control sample duplicates (LCSDs), or MS/MSDs, whichever are analyzed.

The acceptable RPD limits, established in the SAPs (CDM 1999a through d, CDM 2000a, CDM 2000b) for duplicate measurements are in accordance with the laboratory-specific limits; laboratory and analytical methodology; EPA *CLP National Functional Guidelines for Inorganic Data Review* (EPA 1994a); and/or EPA *CLP National Functional Guidelines for Organic Data Review* (EPA 1994b), whichever are applicable.

4.6.1.2 Accuracy

Accuracy is the degree of agreement of a measurement with an accepted reference or true value and is a measure of the bias in a system. Accuracy is quantitative and usually expressed as the percent recovery (%R) of a sample result. Percent recovery is calculated as follows:

$$\text{Percent Recovery} = \text{SSR} - \text{SR} / \text{SA} \times 100$$

Where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added

Ideally, it is desirable that the reported concentration equals the actual concentration present in the sample. Data may be evaluated for accuracy using (in order of priority) LCS/LCSDs, MS/MSDs, and/or surrogates as specified by Appendix B.

The acceptable %R limits are also presented in the projects' SAPs and are in accordance with the laboratory-specific limits, laboratory or analytical methodology, EPA National Functional Guidelines for Inorganic Data Review (EPA 1994a), and/or EPA National Functional Guidelines for Organic Data Review (EPA 1994b), whichever are applicable.

4.6.1.3 Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent:

- The characteristic being measured
- Parameter variations at a sampling point
- An environmental condition

Representativeness is a qualitative and quantitative parameter that is most concerned with the proper sampling design and the absence of cross contamination of samples. Acceptable representativeness is achieved through: (1) careful, informed selection of sampling sites, (2) selection of testing parameters and methods that adequately define and characterize the extent of possible contamination and meet the required parameter reporting limits, (3) proper gathering and handling of samples to avoid interferences and prevent contamination and loss, and (4) collection of a sufficient number of samples to allow characterization. Representativeness was assessed qualitatively by reviewing the selection of sampling sites, testing methods, sensitivity, and number of samples and quantitatively by reviewing the holding times, preservation, and blank samples. If an analyte is detected in a method, preparation, trip, or rinsate blank, any associated positive result less than five times (10 times for common laboratory contaminants) may be considered a false positive. Holding times and preservation were evaluated to determine if analytical results are representative of sample concentrations.

For the RI, samples were collected and analyzed in accordance with the governing SAPs and, therefore, the location, number, and testing methods of the samples were approved by EPA and the stakeholders. Through this review and approval process, it is assumed that the location, number, and testing methods will provide a statistically sound quantification of chemical conditions in the estuary and is representative of actual conditions.

4.6.1.4 Completeness

Completeness is a measure of the amount of usable data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions. Usability was determined by evaluation of the PARCC parameters, excluding completeness. Those data that are validated or evaluated and are not considered estimated or are qualified as estimated or non-detect are usable. Rejected data are not usable. A completeness goal of 90 percent was established for the entire project. Completeness is calculated using the following equation:

$$\% \text{ Completeness} = (\text{DO}/\text{DP}) \times 100$$

Where:

DO = Data obtained and usable

DP = Data planned to be obtained

After review, a completeness of 92 percent was calculated, which achieved the 90 percent completeness goal for the RI.

4.6.1.5 Comparability

Comparability is a qualitative parameter. Consistency in the acquisition, handling, and analysis of samples is necessary for comparing results. Data developed under this investigation were collected and analyzed using standard EPA analytical methods and QC to ensure comparability of results with other analyses performed in a similar manner. Therefore, the data for this RI are considered comparable to the post-1992 historical concentration data. Comparability to the historical data is limited in that detection limits and reporting limits for the historical data are typically not available.

4.6.2 Data Quality Objectives Summary

The final step of the data quality assessment is to determine if the data collected satisfy the project's DQOs and goals. The DQO process is described in the Calcasieu RI SAPs (CDM 1999a, 1999b, 1999c, 1999d, 2000a, 2000b).

The DQO process specifies project decisions, the data quality required to support those decisions, specific data types needed, data collection requirements, and analytical techniques necessary to generate the specified data quality. The process also ensures that the resources required to generate the data are justified. The DQO process consists of seven steps of which the output from each step influences the choices made. Tables 4-7 through 4-10 illustrate the target detection limits for Phases I and II and the target detection limits achieved. Table 4-11 summarizes the project DQOs and provides an assessment of how the project DQOs were met.

4.7 Deviations from Sampling and Analysis Plans

Due to the extent, variability, and complexity of the Calcasieu Estuary RI, unexpected field conditions or other extenuating circumstances required field changes or variances outlined in the SAPs. Program modifications were typically discussed and approved by EPA prior to implementation. Those not discussed with EPA did not affect the project's DQOs for any of the field investigations. Table 4-12 outlines these deviations and impacts, if any, upon the various field investigations.

4.8 Data Interpretation and Analysis

Data generated from the RI were collected in order to describe the concentrations, fate, transport, and impacts of contaminants within the Calcasieu Estuary. In the following sections, subsets of the data based on media, AOC, and energy area were examined to describe the geochemical fate and transport of contaminants in the estuary.

Section 4.8.1 addresses key issues in development of the data sets, and Section 4.8.2 discusses the technical approach to interpret and present the data.

4.8.1 Data Set

The following key issues concerning the data set are discussed in this section:

- Data validation results
- Data collection time frame
- Handling of duplicate samples
- Handling of re-sampled locations
- Handling of split samples
- Handling of sample depths
- Handling of non-detection and estimated concentration values
- Handling of missing total organic carbon and grain size information

4.8.1.1 Data Validation Results

Data validation results were addressed in Section 4.6, Data Validation. A summary of data acceptance and rejection from analysis is provided in the data evaluation summary reports (CDM 2000a, 2002a).

4.8.1.2 Time Frame

Data obtained for the Calcasieu Estuary RI was collected from December 1999 through December 2000, with three distinct sampling events: Phase I (December 1999 to March 2000), sitewide ecological reconnaissance (April to May 2000) and Phase II

(November 2000 to December 2000). For the purpose of nature and extent characterization, all the data collected is considered from the same time period.

4.8.1.3 Duplicate Samples

Duplicate samples were collected and analyzed to provide a check for sampling and analytical error. Duplicate samples are split samples of one homogenized sample volume. Conducting statistical or geostatistical analyses of both the normal and duplicate samples in an area would bias the chemistry at that location by counting the value twice for one location.

To remove this bias, the duplicate sample can be removed, the two values averaged, or a rule created to use the highest detection or lowest non-detection value. For this data set, highest detection/lowest non-detection was used. Therefore, for any sample location where there are two results reported, the highest detected value for each analyte will be used for analysis. Also, for any given location, if it has two values for an analyte that were non-detected, the lowest non-detected value will be used. All remaining duplicate results were removed from the data set.

4.8.1.4 Re-Sampled Sediment Locations

Selected sample locations may have been re-sampled to determine vertical extent, achieve a lower detection limit, or confirm detections. Since sampling was considered collected over the same period, the guideline for re-sampled locations is the same as for duplicate samples with the data set, including either the highest detection or lowest non-detection value.

4.8.1.5 Split Samples

At the request of stakeholders and PRPs, some samples were split externally between PRPs and internally to different laboratories. The results from those analyses resulted in multiple data sets for a single location.

Split samples with PRPs were excluded from the data set since they were not validated by CDM and the detection limits tended to be higher. Internal splits (splits collected by CDM but sent to different laboratories) were handled as regular samples and followed the guidelines of highest detection or lowest non-detection value to be included in the data set.

4.8.1.6 Sampling Depths

Samples were collected at various depths throughout the estuary with surface sediment samples defined as either 0 to 10 or 0 to 15 cm. Multi-depth samples were typically defined as 0 to 10, 10 to 20, and 20 to 30 cm, with the exception of Bayou Verdine. Samples in Bayou Verdine were primarily collected by Conoco who chose to sample at 0 to 15, 15 to 30, and 30 to 45 cm.

For the purpose of horizontal extent, surface sediment was defined as those sediments collected between 0- and 15-cm interval across the entire estuary. For vertical extent, each AOC will be analyzed separately based upon the intervals sampled.

4.8.1.7 Non-detects and Estimated Values

Data generated from chemical analysis may include analyte concentration results that fall below the detection limit of the instrument. These values are described as non-detections of non-detects, and the appropriate detection limit is listed for its value. These non-detects are generally considered to fall somewhere between zero and the detection limit. Approaches to handle non-detects include:

- Set the concentration of the non-detect equal to zero
- Set the concentration of the non-detect equal to the detection limit or
- Non-detect values are assigned one-half the detection limit

Each of the above approaches tends to bias the data either lower, with values equal zero, or higher, with values equal to the detection limit.

Typically for risk assessment purposes, non-detect values are assigned one-half the detection limit. For the nature and extent characterization, one-half the detection limit was used as well to limit as much bias as possible. This approach is recommended by EPA (EPA 1989, 1992) for other types of statistical analysis.

Due to high moisture content in the sediment, many of the non-detected values were extremely high. The guideline for these results was to exclude any results where one-half the detection limit was higher than the minimum value of the detected population. Although these samples may have contaminants present, using extremely high non-detects would add bias to any statistical analysis of the data.

As previously noted, estimated concentrations (i.e., values qualified as J) are considered detects. Their values are usually used with some caution in any manipulation or assessment of the data.

4.8.1.8 Handling of Limited Total Organic Carbon and Grain Size

TOC and grain size are important sediment characteristics in determining the fate and transport of sediment contamination. However, these parameters were not analyzed at every location. These parameters were assumed consistent over a small area typically defined by a reach. The geometric means of these parameters are considered representative of that reach. If a sample had TOC and grain size values, these values were used for that location.

4.8.1.9 Summation of Compounds

Contaminants within a particular chemical group (such as PAHs) are frequently summed to describe a large number of contaminants. In this RI, total PCBs, low molecular, high molecular and total PAHs, (LPAHs, HPAHs, and TPAHs) and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxicity equivalents (2,3,7,8-TCDD TEQ) are used to present the data observed in the estuary.

4.8.1.9.1 PCBs

Total PCBs were calculated by summing the aroclors measured at that location. Non-detects were included in the summation as one-half the detection limit.

4.8.1.9.2 PAHs

LPAHs, HPAHs, and TPAHS are calculated by summing the detected compounds in a particular group. Table 4-13 presents the classification of PAHs. TPAHs are the summation of both the LPAH and HPAH. Non-detects were excluded due to high detection limits at several locations in the estuary. The high detection limits would have introduced a high bias to the summation results.

4.8.1.9.3 Dioxins/Furans

Dioxins/furans are frequently presented as 2,3,7,8-TCDD TEQ in risk assessments and are useful to describe the distribution of dioxins observed. The TEQ is developed by multiplying the concentration for the dioxin or furan by a factor (Table 4-14) and then summing up the results. Non-detects were included in this calculation at one-half the detection limit.

4.8.2 Technical Approach

The primary goal of the RI is to assess whether, and to what extent, sediments and surface water are contaminated or have the potential to adversely affect the environment or human health (EPA 1994). To achieve this end, this document follows the technical approach described below.

- Identify energy areas within each AOC
- Summarize statistics of results within each energy area in an AOC
- Perform multivariate analyses based on media and energy areas
- Perform a statistical comparison between the reaches and/or energy areas and reference areas

Presentation of data and interpretation results include:

- Summary statistic tables
- Spatial plots using geostatistical methods such as kriging

Interpretation of results will be presented in Sections 7 through 10, which discuss the nature and extent of contamination in each of the AOCs and Section 11, which discusses the results of the tissue analysis.

4.8.2.1 Energy Areas

As stated in Sections 2 and 3, the site was divided into five primary energy settings: bayous, marshes, shallow lakes, shipping channels, and river. The energy of a specific area will influence surface water variability, sediment nature, and stability.

Depositional environment, surface water conditions, and stability of the sediment can be used to describe the behavior of the system as a whole. Exhibit 4-1 lists the data sets created for sediment and surface water. Tissue data sets were based on AOC and grouping as discussed in Section 4.3.

Exhibit 4-1 Data Sets for Sediment and Surface Water

| Area of Concern | Energy Area |
|-----------------|--------------|
| Bayou D'Inde | Bayou |
| Bayou D'Inde | Marsh |
| Bayou Verdine | Bayou |
| Lower Calcasieu | Bayou |
| Lower Calcasieu | Other |
| Lower Calcasieu | Shallow Lake |
| Lower Calcasieu | Ship Channel |
| Upper Calcasieu | Bayou |
| Upper Calcasieu | Marsh |
| Upper Calcasieu | River |
| Upper Calcasieu | Shallow Lake |
| Upper Calcasieu | Ship Channel |
| Reference Area | Bayou |

4.8.2.2 Summary Statistics

Summary statistics were generated for each of the data sets using Microsoft Excel and the Caltrans Data Analysis Tool (DAT). The Caltrans DAT calculates summary statistics for data sets that include not detected data using regression on order statistics (ROS). The DAT includes a Visual Basic program that models the statistical procedures presented in Shumway and Azari (2000), Helsel (1990), and Helsel and Cohn (1988). The DAT has been verified against results published in those references.

The ROS method develops probability-plotting positions for each data point (censored and uncensored) based on the ordering of the data. A least squares line is then fit by regressing the log transformed concentrations to the uncensored probability plotting positions. The censored data points are assigned concentrations for calculation of summary statistics based on their probability plotting positions and the regression line equation. Summary statistics are calculated based on the uncensored data points and the "filled-in" censored values. Variance summary statistics are calculated using a Tukey-Jackknife algorithm. The jackknife procedure is performed by sequentially removing one point from the data set, running the analysis, and calculating the variance estimators as the average of each of the "n" runs of data.

4.8.2.3 Multivariate Analyses

Multivariate refers to the analysis of data consisting of two or more random variables. Multivariate analysis was used for the RI data sets because the complex interactions between variables are difficult to isolate and study individually. The sediment data

sets were statistically analyzed using principal components analysis (PCA). PCA will be used to reduce the multidimensionality of the data sets (Chapman 1996) and is a type of exploratory data analysis technique designed to:

- Study the correlations of multivariate data sets by grouping variables or loadings (e.g., pH and zinc in sediment) that show similar tendencies in factors. The first factor accounts for as much of the variability in the data as possible and each succeeding component accounts for as much of the remaining variability as possible.
- Reveal a simple underlying structure within a set of multivariate data. Such interpretation may provide useful information regarding geochemical fate and transport.
- Summarize many variables by a few factors. Essentially this is a data reduction technique whereby several original variables may be represented by one or a few indicator variables or by the factor itself that may be used as a predictor or criterion in subsequent analysis.

The goal of PCA is to summarize a multivariate data set as accurately as possible using a few factors. Each factor is a new axis through the multivariate data that represents the best association between a number of the variables (similar to a regression line). PCA provides the correlations between each factor and each variable and the relative amount of the total data set variance apportioned to or explained by each factor. Thus, in practice, PCA results are used to identify the original variables that load high within a particular factor and the percentage of the total variance explained by that factor. Exhibit 4-2 summarizes the data sets created for surface (0 to 10 cm) sediment.

Exhibit 4-2 Surface Sediment (0 to 10 cm) Data Sets for PCA

| PCA Data | Area of Concern | Energy Area | Samples ¹ | Constituents ² |
|----------|-----------------|--------------|----------------------|---------------------------|
| 1 | Bayou D'Inde | Bayou | 100 | 140 |
| 2 | Bayou D'Inde | Marsh | 161 | 144 |
| 3 | Bayou Verdine | Bayou | 78 | 90 |
| 4 | Lower Calcasieu | Bayou | 18 | 33 |
| 5 | Lower Calcasieu | Other | 7 | 48 |
| 6 | Lower Calcasieu | Shallow Lake | 76 | 75 |
| 7 | Lower Calcasieu | Ship Channel | 52 | 63 |
| 8 | Upper Calcasieu | Bayou | 9 | 33 |
| 9 | Upper Calcasieu | Marsh | 8 | 35 |
| 10 | Upper Calcasieu | River | 12 | 32 |
| 11 | Upper Calcasieu | Shallow Lake | 46 | 79 |
| 12 | Upper Calcasieu | Ship Channel | 54 | 75 |
| 13 | Reference Area | Bayou | 18 | 37 |
| TOTAL | | | 639 | |

¹ Number of samples with a result for at least one constituent in the AOC/Each data set.

² Number of constituents (variables) with a least 3 detections.

4.8.2.3.1 Steps in PCA

For each data set shown in Exhibit 4-2, PCA involved the following steps:

- A Pearson correlation matrix was generated to evaluate the numbers of data pairs for each constituent in the data set.
- Starting with the constituents with the highest number of data points, an initial PCA was conducted.
- Constituents with lower numbers of data points were added iteratively and additional PCAs conducted. The additional constituents were retained in subsequent PCAs if the requirement of a minimum of three data pairs was maintained.
- The PCA that allowed the largest number of constituents was retained as the result. In some cases, this meant removing a constituent with a larger number of cases in lieu of several constituents with lower numbers of cases.

The above steps were necessary to accommodate the holes in the data sets due to samples not being analyzed for every constituent (i.e., sampling for only dioxin/furans at selected locations). The PCAs were conducted using SYSTAT Version 10.0 (SPSS Software) with the following parameters:

- *Pairwise* deletion of missing cases to allow inclusion of the maximum number of variables (constituents).
- *Varimax* rotation of factors to minimize the number of variables that have high loadings on each factor (also known as factor simplification).
- Number of factors = 5. This number was selected based on preliminary PCA results that indicated at least 80 percent of the total variance was explained by the first five factors.

4.8.2.3.2 PCA Result Presentation

The PCA results for each of the 13 data sets were tabulated and graphed for ease of interpretation. Results included the percentage of the total variance explained and the factor 1 through factor 5 loadings for each constituent. In addition, a constituent ranking system was developed to support selection of indicators for subsequent statistical analysis. The ranking system consisted of the following:

Rank = (variance explained by factor) x (factor loading) x (relative sample size)

In this expression, “variance explained by factor” is the fraction of the total variance, and “relative sample size” is the number of results for the constituent in the data set divided by the total number of samples. For each data set, five sets of ranks were determined for each constituent (one set for each of the five factors), and the five ranks for each constituent were then summed. Thus, one set of ranks was developed

for each of the 13 data sets. Results of the PCA will be presented in Sections 7, 8, 9, and 10.

4.8.2.4 Comparison of Data to Reference Areas

Deciding whether site concentration levels tend to be larger than background or reference area concentrations can be answered by using statistical tests. Selecting the appropriate statistical test should look at the number of samples required for each of the various tests to achieve DQOs, the particular distribution (normal or lognormal) expected of the data to be collected, and information in published statistical papers that demonstrate the performance of the candidate tests for various data distributions and contamination scenarios (Naval Facilities Engineering Command [NFEC] 1999).

The Wilcoxon Rank Sum (WRS) Test evaluates whether there is a statistically significant difference between the medians of two data sets (i.e., the null hypothesis [H_0] that the populations from which the two data sets have been drawn have the same mean is tested against the alternative [H_A] that the populations have different means). The WRS Test is described in Gilbert (1987) and EPA (1992). The test was conducted on sediment samples using the computer program Systat V.10.

The WRS Test is a nonparametric statistical test that does not require the assumption that the data sets are derived from a normal population distribution. The only assumption is that the distributions of the two populations have the same shape, although they need not be symmetric. The WRS test was selected (over the parametric t test equivalent) because the population distributions were unknown and the sample data sets were generally insufficient to recognize the shapes of the population distributions. In addition, the WRS test is capable of handling the moderate number of nondetect values present in the sample data sets.

To ensure consistency, the sediment sample data sets used for the WRS testing were obtained using the same protocols used in the PCA. As with the PCA, the data sets were 13 groups as presented in Exhibit 4-1. The constituents selected for the WRS testing were determined from the PCA results. Essentially, those constituents with the highest PCA rankings (most important) were selected, with the exception of 2,3,7,8-TCDD TEQ, which was not used in the PCA.

At the conclusion of Sections 7, 8, 9, and 10, results from this analysis will be presented.

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